

Coutinhoite, a new thorium uranyl silicate hydrate, from Urucum mine, Galiléia, Minas Gerais, Brazil

DANIEL ATENCIO,^{1,*} FLÁVIO M.S. CARVALHO,¹ AND PAULO A. MATIOLI²

¹Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 São Paulo, SP, Brazil

²Museu Jobas de Ciências Naturais “José Bonifácio de Andrada e Silva,” Rua Martim Afonso 24, Biquinha, 11310-010 São Vicente, SP, Brazil

ABSTRACT

The new mineral coutinhoite, ideally $\text{Th}_x\text{Ba}_{(1-2x)}(\text{H}_2\text{O})_y(\text{UO}_2)_z\text{Si}_5\text{O}_{13}\cdot\text{H}_2\text{O}$, with $0 \leq x \leq 0.5$ and $0 \leq y \leq (2 + x)$, occurs as a secondary hydrothermal mineral in the Córrego do Urucum granitic pegmatite, Lavra Urucum, Galiléia Co., Minas Gerais, Brazil. Coutinhoite is intimately associated with weeksite, phosphuranylite, meta-uranocircite, and uranocircite on muscovite and microcline. The mineral forms irregular aggregates with very small curved scales, flaky crystals, up to 10 μm long and with a thickness up to about 0.5 μm . Coutinhoite is transparent to translucent and displays a waxy to silky luster; color and streak are yellow. It is non-fluorescent. The hardness is less than 2. It is brittle. Calculated density is 3.839 g/cm^3 . Coutinhoite is biaxial negative, α 1.620(3), β 1.627(3), γ 1.629(3), $2V_{\text{meas.}} = 40(5)^\circ$, $2V_{\text{calc.}} = 56.1^\circ$, dispersion $r < v$ strong, orientation $Y = c$. Pleochroism is $Z > Y$, X yellow. The empirical formula (based on $\text{Si} + \text{P} = 5$) is $(\text{Th}_{0.30}\text{Ba}_{0.19}\text{K}_{0.07}\text{Ca}_{0.04})_{\Sigma 0.60}(\text{UO}_2)_{2.00}(\text{Si}_{4.92}\text{P}_{0.08})_{\Sigma 5.00}\text{O}_{12.91}\cdot 2.86\text{H}_2\text{O}$. The mineral is orthorhombic, probable space group $Cmmb$ (67). Cell parameters were refined from the powder data: a 14.1676(9), b 14.1935(9), c 35.754(2) Å, $V = 7189.7(2)$ Å³, and $Z = 16$. It is probably isostructural with weeksite. Both the description and name were approved by the CNMMN-IMA (Nomenclature Proposal 2003-025).

INTRODUCTION

The importance of uranium mineralogy to understanding the genesis of uranium deposits, as well as for environmental applications, was emphasized by Jackson and Burns (2001). Uranyl compounds that may form by the alteration of nuclear waste will incorporate radionuclides into their structures, thereby retarding their release. Uranyl silicates (e.g., uranophane, uranophane-beta, boltwoodite, haiweeite, weeksite) are likely to be abundant in a geological repository for nuclear waste, owing to the alteration of spent nuclear fuel and borosilicate waste glass in the presence of silicon derived from repository host-rocks. Thus, an understanding of the structures of uranyl silicates may be a key to understanding the long-term performance of a geological repository for nuclear waste. Coutinhoite is a thorium uranyl silicate probably isostructural with weeksite. The weeksite structure would be then an important depository of Th^{4+} .

The first coutinhoite samples were collected by one of us (P.A.M.) in 1997. Additional material was obtained in 2003. The mineral is very rare. Both description and name were approved by the CNMMN-IMA (Nomenclature Proposal 2003-025). The mineral is named in honor of José Moacyr Vianna Coutinho (born 1924), Professor of Mineralogy and Petrography at the Instituto de Geociências of Universidade de São Paulo, Brazil, who has made significant contributions to Brazilian mineralogy and geology. Holotype material is deposited under the number DR523 in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080, São Paulo, SP, Brazil and in the Museu Jobas de Ciências Naturais

“José Bonifácio de Andrada e Silva,” Rua Martim Afonso, 24, Biquinha, 11310-010, São Vicente, SP, Brazil.

OCCURRENCE

Coutinhoite occurs as a secondary hydrothermal mineral in the Córrego (= creek) do Urucum granitic pegmatite, Lavra (= mine) Urucum (also known as Lavra do Tim), Galiléia Co. (19°0'S 41°32'W, DMS), Minas Gerais, Brazil. This pegmatite was studied by Cassedanne (1986) and Cassedanne et al. (1986), who described the following minerals: quartz, albite, microcline, muscovite, biotite, beryl, spodumene, elbaite, schorl, fluorapatite, spessartine, titanite, microlite, cassiterite, stokesite, löllingite, uraninite, tennantite, covellite, pyrite, bismuth, sulfur, montmorillonite, nontronite, dickite, cookeite, opal, hematite, goethite, hörnesite, karibibite, schneiderhöhnite, scorodite, pharmacosiderite, vivianite, phosphosiderite, phosphuranylite, saléite,

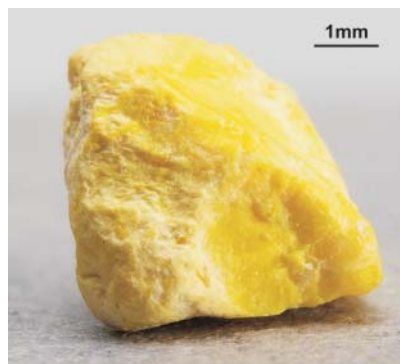


FIGURE 1. Irregular aggregate of coutinhoite from Urucum mine, Galiléia, Minas Gerais, Brazil.

* E-mail: datencio@usp.br

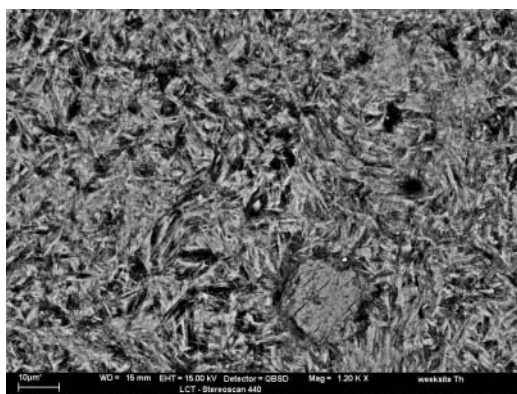


FIGURE 2. Back-scattered electron image of coutinhoite.

wölsendorffite, amorphous iron arsenates, and an amorphous uranium arsenate with Fe and Th. Coutinhoite is intimately associated with weeksite, phosphuranylite, meta-uranocircite and uranocircite on muscovite and microcline. The uranium and thorium in coutinhoite are products of the oxidation of uraninite.

APPEARANCE AND PHYSICAL PROPERTIES

The mineral forms irregular aggregates (Fig. 1) with very small curved scales, flaky crystals (Fig. 2), up to 10 μm long and a thickness up to about 0.5 μm . Well-shaped crystals were not observed. Twinning was not observed. Coutinhoite is transparent to translucent and displays a waxy to silky luster; the color and streak are yellow. It is non-fluorescent under both short- (254 nm) and long-wave (366 nm) ultraviolet radiation. The hardness is less than 2. It is brittle. The cleavage and fracture are not determinable. The density was not measured due to the paucity of material; the calculated density is 3.839 g/cm^3 .

OPTICAL PROPERTIES

Optical data for coutinhoite were determined in white light. The indices of refraction were measured by immersion of grains in liquids calibrated with the Abbé refractometer. Coutinhoite is biaxial negative, α 1.620(3), β 1.627(3), γ 1.629(3), $2V_{\text{meas.}} = 40(5)^\circ$, $2V_{\text{calc.}} = 56.1^\circ$, dispersion $r < v$ strong, orientation $Y = c$. The crystals are too narrow to determine the complete optical orientation. The pleochroism is $Z > Y$, X yellow.

CHEMICAL DATA

Chemical analyses (55) were carried out by means of an electron microprobe (WDS mode, 15 kV, 20 nA, 1 μm beam diameter). The chemical analyses were done at the Instituto de Geociências of the Universidade de São Paulo using a JEOL JXA-8600 electron microprobe and a Noran system for automation and data reduction. A coutinhoite aggregate was embedded in epoxy resin and polished. Given the small size of the crystals and relatively high water content, we expected that it could be unstable under the electron beam. In order to minimize deterioration, the appropriate analytical conditions were selected. No significant damage was seen. The mean analytical results are represented in Table 1. No elements with $Z > 8$, other than those reported herein, were indicated by EDS. The presence of H_2O was identified from an IR spectrum (Fig. 3) obtained at the Instituto de Química of the Universidade de São Paulo,

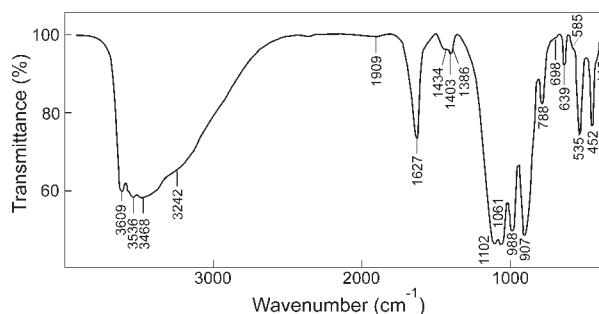


FIGURE 3. Infrared spectrum of coutinhoite.

TABLE 1. Chemical composition of coutinhoite from the Urucum mine

Constituent	wt%	Range	Standard deviation	Probe standard
ThO_2	7.72	4.60–13.12	0.3	ThO_2
BaO	2.81	2.51–3.27	0.2	celtsian
K_2O	0.32	0.17–0.56	0.02	orthoclase
CaO	0.23	0.17–0.30	0.02	anorthite
UO_3	54.94	51.62–57.77	1.2	UO_3
SiO_2	28.44	26.19–30.31	0.15	ThSiO_4
P_2O_5	0.58	0.24–0.95	0.05	synthetic chlorapatite
H_2O	(4.96)	3.46–7.95		
Total	(100.00)			

and the amount was calculated by difference. Some comments on the infrared spectrum can be made. There may be several structurally different and nonequivalent water molecules in the structure of coutinhoite. However, the chemistry of OH groupings in its structure may be different. The wavenumber of the band at 1627 cm^{-1} (assigned to the bending vibration of H_2O) indicates that water molecules are present in the structure. The sharp band at 3610 cm^{-1} may indicate that, e.g., free or only weakly hydrogen-bonded water molecules are also present or this band may be connected with the OH-stretching vibrations of free hydroxyl ions present in the structure of coutinhoite, as observed in the crystal structure of haiweeite (Burns 2001). The other two broad bands at 3536 and 3468 cm^{-1} with a shoulder at 3242 cm^{-1} may in fact be assigned to OH-stretching vibrations of water molecules. It is not clear if only water molecules, or water molecules and hydroxyl groups are present in the crystal structure of coutinhoite. The IR spectrum of coutinhoite is similar to that of weeksite. Based on an IR spectrum, Plesko et al. (1992) also suspected the presence of OH or H_2O in weeksite, but these were not found in the crystal structure studies by Baturin and Sidorenko (1985) and Jackson and Burns (2001). Perhaps the same could be applied to coutinhoite

The empirical formula (based on $\text{Si} + \text{P} = 5$) is $(\text{Th}_{0.30}\text{Ba}_{0.19}\text{K}_{0.07}\text{Ca}_{0.04})_{\Sigma 0.60}(\text{UO}_2)_{2.00}(\text{Si}_{4.92}\text{P}_{0.08})_{\Sigma 5.00}\text{O}_{12.91} \cdot 2.86\text{H}_2\text{O}$. The simplified formula, $\text{Th}_{0.5}(\text{UO}_2)_2\text{Si}_5\text{O}_{13} \cdot 3\text{H}_2\text{O}$, requires ThO_2 12.47, UO_3 54.04, SiO_2 28.38, H_2O 5.11, total 100.00 wt%. A better general formula for coutinhoite may be expressed as $\text{Th}_x\text{Ba}_{(1-2x)}(\text{H}_2\text{O})_y(\text{UO}_2)_2\text{Si}_5\text{O}_{13} \cdot \text{H}_2\text{O}$ with $0 \leq x \leq 0.5$ and $0 \leq y \leq (2+x)$. The simplified general formula may be expressed as $\text{Th}_{0.5}(\text{UO}_2)_2\text{Si}_5\text{O}_{13} \cdot 1-3.5\text{H}_2\text{O}$.

CRYSTALLOGRAPHY

Powder data were obtained by means of a Siemens D5000 diffractometer equipped with a Göbel mirror and a position-sensitive detector using $\text{CuK}\alpha$ radiation and 40 kV and 40 mA

at Instituto de Geociências of the Universidade de São Paulo (Table 2). No metamictization was suggested by the X-ray diffraction data. The mineral is orthorhombic. The space group is not confirmed, so should be referred to as “probable space group”. The space group *Cmmb* (67) was chosen by analogy with the space group of weeksite. Cell parameters were refined from the powder data: *a* 14.1676(9), *b* 14.1935(9), *c* 35.754(2) Å, *V* = 7189.7(2) Å³. *Z* = 16. The *a*:*b*:*c* ratio calculated from the unit-cell parameters is 0.9982:1:2.5190. The Gladstone-Dale compatibility is 1 – (*K_p*/*K_c*) = 0.032, which is excellent.

No single-crystal study was done, due to the crystal dimensions. Although the unit cell of coutinhoite is similar to that of weeksite, we are not completely convinced they are actually

isostructural.

Weeksite was originally described from the Thomas Range, Juab County, Utah, by Outerbridge et al. (1960) as K₂(UO₂)₂Si₆O₁₅·4H₂O. Yermenko et al. (1977) studied two generations of weeksite from Afghanistan. For the first one, the chemical data (methods not specified) indicate the formula (K_{1.04}Na_{0.63}Ca_{0.34}Ba_{0.12}Al_{0.05}Mg_{0.04}Sr_{0.02})_{Σ2.24}(UO₂)_{1.67}(Si₅O_{13.10})·3.35H₂O, and for the second one (K_{1.13}Na_{0.73}Mg_{0.05}Al_{0.04}Ca_{0.01}Sr_{0.01}Ba_{0.01})_{Σ1.98}(UO₂)_{1.86}(Si₅O_{12.93})·3.45H₂O. The authors quoted a set of optical data (α 1.62 to 1.63, γ 1.69 to 1.7) and lattice parameters for a single crystal [monoclinic, *a* 9.63(1), *b* 7.12(1), *c* 7.15(1) Å, β 111°56']. They do not mention if the data are for weeksite from the first or the second generation. Both optical and X-ray data are in disagreement with the traditional data for weeksite.

Baturin and Sidorenko (1985) studied the crystal structure of a weeksite sample from Afghanistan and obtained the formula K₂(UO₂)₂Si₅O₁₃·3H₂O, or in more detail, [K_{0.31}Na_{0.18}(H₂O)_{0.50}]₄(UO₂)₂Si₅O₁₃·H₂O. They found four sites occupied by [K_{0.31}Na_{0.18}(H₂O)_{0.50}] and one by H₂O. Water was determined by ATG. They provided a cell with *Z* = 2 (a subcell) and a final *R* of 12%.

Jackson and Burns (2001) attained a better result for their crystal structure determination of weeksite from the Anderson mine, Yavapai County, Arizona, with *Z* = 16 and a final *R* value of 7.0%. They concluded that the formula is K_{1.26}Ba_{0.25}Ca_{0.12}(UO₂)₂Si₅O₁₃·H₂O, or K₂(UO₂)₂Si₅O₁₃·H₂O. They obtained 1.46H₂O (by difference in order to give an analytical total of 100%) and 1.28H₂O per formula unit by crystal structure determination. For one formula unit, they found two sites partly occupied by K, one site occupied mainly by Ba and H₂O, and one site fully occupied by H₂O. The formula could be expressed as K_{*x*}Ba_{1-(*x*/2)}}(H₂O)_{*y*}(UO₂)₂Si₅O₁₃·H₂O, with 0 ≤ *x* ≤ 2 and 0 ≤ *y* ≤ [2 – (*x*/2)], if we consider the possibility of H₂O at both the K and Ba sites [Baturin and Sidorenko (1985) considered the presence of H₂O at all the K,Na positions]. Consequently it would be possible to have a maximum of 3H₂O per formula unit.

The main difference between the two crystal structure determinations is that Baturin and Sidorenko (1985) found one additional site for K,Na,H₂O. In conclusion, the water content of weeksite can be variable from one to 2H₂O per formula unit (if *x* = 2, i.e., K₂Ba₀ in the formula), or from one to 3H₂O per formula unit (if *x* = 0, i.e., K₀Ba₁ in the formula). In coutinhoite, it can be variable from one to 3.5H₂O per formula unit (if *x* = 0.5, i.e., Th_{0.5}Ba₀ in the formula) or from one to 3H₂O per formula unit (if *x* = 0, i.e., Th₀Ba₁ in the formula).

Weeksite has an open uranyl silicate framework structure, and the most likely location for Th⁴⁺ is in the channels that run through the structure. However, we cannot see how the bonding requirements of Th can be met within the channels, as the apical O atoms of the Si tetrahedra are bridging, and the uranyl ion O atoms can only form weak bonds. The substitution of Th⁴⁺ at a site normally occupied by monovalent (K) or divalent (Ba) cations suggests some considerable restructuring of this site to avoid overbonding of O atoms, presumably involving extra H₂O molecules. Significant distortion of the framework would be expected induced by the incorporation of a strong Lewis base such as Th⁴⁺.

No other uranyl silicates containing Th are known. The only

TABLE 2. X-ray powder-diffraction data for coutinhoite from the Urucum mine

<i>hkl</i>	<i>d_{meas}</i> (Å)	<i>d_{calc}</i> (Å)	<i>h</i>	<i>k</i>	<i>l</i>
45	8.919	8.939	0	0	4
100	7.059	7.097	0	2	0
59	5.563	5.558	0	2	4
23	4.834	4.827	2	2	2
47	4.581	4.560	2	0	6
13	4.470	4.469	0	0	8
48	3.826	3.836	2	2	6
86	3.528	3.548	0	4	0
20	3.326	3.298	0	4	4
57	3.287	3.293	4	0	4
73	3.188	3.192	2	0	10
17	3.141	3.169	4	2	0
46	2.981	2.987	4	2	4
78	2.904	2.911	2	2	10
13	2.790	2.800	2	4	6
14	2.501	2.507	4	4	0
24	2.407	2.402	2	0	14
22	2.371	2.366	0	6	0
27	2.275	2.276	2	2	14
17	2.231	2.226	2	6	2
22	2.192	2.195	6	0	6
8	2.173	2.172	4	2	12
13	2.134	2.131	0	2	16
21	2.096	2.097	6	2	6
17	1.990	1.989	2	4	14
31	1.968	1.967	4	6	0
17	1.917	1.921	4	6	4
37	1.901	1.899	6	2	10
16	1.871	1.867	6	4	6
16	1.828	1.826	4	2	16
13	1.788	1.788	0	0	20
20	1.774	1.771	8	0	0
21	1.735	1.734	6	0	14
22	1.719	1.718	8	2	0
23	1.686	1.686	2	6	14
10	1.653	1.653	2	8	6
13	1.595	1.596	4	0	20
13	1.584	1.585	8	4	0
20	1.558	1.557	4	2	20
8	1.514	1.514	6	6	10
6	1.476	1.477	4	6	16
9	1.456	1.455	4	4	20
11	1.427	1.427	2	8	14
12	1.399	1.398	6	6	16
9	1.389	1.389	0	8	16
9	1.381	1.380	6	8	6
9	1.351	1.350	2	0	26
15	1.318	1.317	10	0	10
12	1.296	1.295	10	2	10
8	1.260	1.259	0	8	20
10	1.240	1.240	6	8	14
6	1.222	1.222	2	10	14
10	1.189	1.188	6	0	26
9	1.171	1.170	10	4	14
8	1.153	1.152	6	10	10

known uranyl thorium mineral is althupite, $\text{AlTh}(\text{UO}_2)[(\text{UO}_2)_3\text{O}(\text{OH})(\text{PO}_4)_2]_2(\text{OH})_3 \cdot 15\text{H}_2\text{O}$ (Piret and Deliens 1987), where Th^{4+} occurs in the interlayer of the structure.

ACKNOWLEDGMENTS

We acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support (Process 2001/05171-0); the members of the Commission on New Minerals and Mineral Names of the International Mineralogical Association (CNMMN-IMA) for their helpful suggestions and comments; J.M.V. Coutinho for assistance with determination of optical properties; M. Mansueto for assistance with the microprobe analysis; O. Andrade, O. Andrade Filho, and I.C. Andrade, from the Urucum mine; and L. Groat, S. Krivovichev, and an anonymous reviewer for their constructive comments.

REFERENCES CITED

- Baturin, S.V. and Sidorenko, G.A. (1985) Crystal structure of weeksite ($\text{K}_{0.62}\text{Na}_{0.38}$) $_2(\text{UO}_2)_2[\text{Si}_4\text{O}_{13}] \cdot 3\text{H}_2\text{O}$. *Soviet Physics Doklady*, 30, 435–437.
- Burns, P.C. (2001) A new uranyl silicate sheet in the structure of haiweeite and comparison to other uranyl silicates. *Canadian Mineralogist*, 39, 1153–1160.
- Cassedanne, J.P. (1986) The Urucum pegmatite, Minas Gerais, Brazil. *Mineralogical Record*, 17, 307–314.
- Cassedanne, J.P., Cassedanne, J.O., and Carvalho, H.F. (1986) Löllingite, uraninite et produits de leur altération dans la pegmatite de l'Urucum (Minas Gerais). *Anais da Academia Brasileira de Ciências*, 58, 249–266.
- Jackson, J.M. and Burns, P.C. (2001) A re-evaluation of the structure of weeksite, a uranyl silicate framework mineral. *Canadian Mineralogist*, 39, 187–195.
- Outerbridge, W.F., Staatz, M.H., Meyrowitz, R., and Pommer, A.M. (1960) Weeksite, a new uranium silicate from the Thomas Range, Juab County, Utah. *American Mineralogist*, 45, 39–52.
- Piret, P. and Deliens, M. (1987) Les phosphates d'uranyle et d'aluminium de Kobokobo IX. L'althupite $\text{AlTh}(\text{UO}_2)[(\text{UO}_2)_3\text{O}(\text{OH})(\text{PO}_4)_2]_2(\text{OH})_3 \cdot 15\text{H}_2\text{O}$, nouveau mineral; propriétés et structure cristalline. *Bulletin de Minéralogie*, 110, 65–72.
- Plesko, E.P., Scheetz, B.E., and White, W.B. (1992) Infrared vibrational characterization and synthesis of a family of hydrous alkali uranyl silicates and hydrous uranyl silicate minerals. *American Mineralogist*, 77, 431–437.
- Yeremenko, G.K., Il'menov, Ye.S., and Azimi, N.A. (1977) Find of weeksite-group minerals in Afghanistan. *Doklady Akademii Nauk SSSR*, 237, 226–228.

MANUSCRIPT RECEIVED AUGUST 15, 2003

MANUSCRIPT ACCEPTED NOVEMBER 26, 2003

MANUSCRIPT HANDLED BY LEE GROAT